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MONOGRAPHS ON MINERAL RESOURCES
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MONOGRAPHS ON MINERAL RESOURCES
WITH SPECIAL REFERENCE TO THE
BRITISH EMPIRE

PREPARED UNDER THE DIRECTION OF THE
MINERAL RESOURCES COMMITTEE OF THE
IMPERIAL INSTITUTE

BISMUTH ORES

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WITH A MAP



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IMPERIAL INSTITUTE

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THE Mineral Resources Committee of the Imperial Institute has arranged for the issue of this series of Monographs on Mineral Resources in amplification and extension of those which have appeared in the *Bulletin of the Imperial Institute* during the past fifteen years.

The Monographs are prepared either by members of the Scientific and Technical Staff of the Imperial Institute, or by external contributors, to whom has been available the statistical and other special information relating to mineral resources collected and arranged at the Imperial Institute.

The object of these Monographs is to give a general account of the occurrences and commercial utilization of the more important minerals, particularly in the British Empire. No attempt has been made to give details of mining or metallurgical processes.

HARCOURT,
Chairman, Mineral Resources Committee.

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CONTENTS

CHAPTER I

BISMUTH ORES: THEIR OCCURRENCE, CHARACTERS AND USES

PAGE
I

CHAPTER II

SOURCES OF SUPPLY OF BISMUTH ORES

(a) BRITISH EMPIRE :

<i>Europe</i> : England ; Scotland	22
<i>Asia</i> : India	23
<i>Africa</i> : Northern Rhodesia ; Southern Rhodesia ; Union of South Africa	24
<i>North America</i> : Canada	25
<i>Australasia</i> : Australia ; New Zealand	26

CHAPTER III

SOURCES OF SUPPLY OF BISMUTH ORES (*continued*)

(b) FOREIGN COUNTRIES :

<i>Europe</i> : Austria ; Czechoslovakia ; France ; Germany ; Norway ; Sweden ; Rumania ; Russia ; Switzerland ; Yugo-Slavia	35
<i>Asia</i> : China ; Dutch East Indies ; Japan ; Korea (Chosen) ; Siberia	40
<i>North America</i> : Mexico ; United States	42
<i>South America</i> : Argentina ; Bolivia ; Brazil ; Chile ; Peru ; Venezuela	48
WORLD MAP OF BISMUTH DEPOSITS	55
REFERENCES TO LITERATURE ON BISMUTH	57

NOTE: Numerals in square brackets in the text refer to the
Bibliography at the end.

BISMUTH ORES

CHAPTER I

BISMUTH ORES: THEIR OCCURRENCE, CHARACTERS AND USES

INTRODUCTION

BISMUTH, a metal very uncommon in nature, does not appear to have been known to the ancients, but in the Middle Ages it became quite familiar, although often confused with other metals—antimony, zinc, tin, lead, etc.—probably on account of the impurity of the specimens available. Its elementary nature was not understood for some time.

Metallic bismuth was first known as *marcasite*. Later in 1450 it was described as a metal by Basil Valentine, who called it *wismut* (white matter). Paracelsus termed it *wissmat*, and in allusion to its brittle nature called it a "bastard" or "half metal." Georgius Agricola, about 1550, described it as *wissmuth*, latinized to *bisementum*, but also used the term *plumbum cinerarium*. In 1597 Andreas Libavius mistook it for antimony, and in 1675 Nicholas Lemery confused it with zinc. The metal was first accurately described by the Swedish chemist, T. O. Bergman, about 1779.

Bismuth is somewhat limited as regards its applications and consequently there is only a small demand for it, so that in order not to overstock the market, mining operations are only conducted on a comparatively small scale [1] [2].

BISMUTH MINERALS

The few bismuth minerals of economic importance are given in the following table:

BISMUTH ORES

Class.	Name.	Formula.	Bismuth.	Specific gravity.	Hardness.	Whether Primary or Secondary.
Native metal.	Native bismuth	Bi	% 95-99.9	9.7-9.8	2-2.5	P, S
Oxide	Bismuth ochre or bismite	Bi_2O_3	89.6 79.1	4.3 6.9	very soft	S
Carbonate	Bismutite	$\text{Bi}_2(\text{OH})_4\text{CO}_3$			very soft	S
Sulphide	Bismuthinite	Bi_2S_3	81.2	6.4-6.5	2	P, S

Native bismuth is the commonest ore-mineral. It is found usually in reticulated or feathery shapes or in granular masses with a crystalline structure. Native crystals, which are rhombohedral, are rare and ill-defined. In colour the mineral is silver-white with a reddish tinge. It sometimes contains traces of sulphur, arsenic, tellurium, etc.

Bismuthinite, next in importance, crystallizes in the rhombic system in small needle like crystals; usually, however, it is massive. Its colour is lead-grey to tin-white, and its lustre, metallic. It greatly resembles stibnite (Sb_2S_3), with which it is isomorphous.

Bismuth ochre is of a yellowish colour and has an earthy appearance. It is a surface mineral and is often intermixed with iron, copper and arsenic oxides.

Bismutite is also of an earthy nature, and is of a greyish-yellow or greenish colour. It is often found in association with the ochre, being also a surface mineral.

Bismuth ochre and bismutite are both secondary minerals derived from the primary minerals bismuthenite and native bismuth. They occur mostly as incrustations covering other minerals.

Other bismuth minerals, but unimportant as sources of bismuth, are :

Bismutospharite, the anhydrous carbonate, $2\text{Bi}_2\text{O}_3 \cdot \text{Bi}_2(\text{CO}_3)_3$; *tetradymite*, the sulpho-telluride, $\text{Bi}_2(\text{TeS})_3$; *montanite*, a basic tellurate, $\text{Bi}_2(\text{OH})_4 \cdot \text{TeO}_4$; *eulytite* and *agricolite*, silicates, $\text{Bi}_4(\text{SiO}_4)_3$; *atelesite*, basic bismuth arsenate, $3\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$; *pucherite*, the vanadate, $\text{Bi}_2\text{O}_3 \cdot \text{V}_2\text{O}_5$; *wittichenite*, copper-

THEIR OCCURRENCE, CHARACTERS AND USES 3

bismuth glance, $3\text{Cu}_2\text{S} \cdot \text{Bi}_2\text{S}_3$; *aikinite* or *patrinite*, needle ore, $(\text{Pb}, \text{Cu})_2\text{S} \cdot \text{Bi}_2\text{S}_3$; *cosalite*, lead-bismuth sulphide, $2\text{PbS} \cdot \text{Bi}_2\text{S}_3$; another lead-bismuth sulphide, *bismuto-plagionite*, $5\text{PbS} \cdot 4\text{Bi}_2\text{S}_3$; *mplectite*, copper-bismuth sulphide, $\text{CuS} \cdot \text{Bi}_2\text{S}_3$; *kobellite*, lead-bismuth-antimony sulphide, $2\text{PbS} \cdot (\text{Bi}, \text{Sb})_2\text{S}_3$; *guanajuatite*, a selenide, Bi_2Se_3 ; *walpurgite*, a basic arsenate of bismuth and ranium, $5\text{Bi}_2\text{O}_3 \cdot 3\text{UO}_3 \cdot 2\text{As}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$; *chilenite*, a native bismuth-silver alloy, Ag_6Bi ; and *maldonite*, bismuth gold, Au_2Bi . *Ilaonite*, is not a homogeneous mineral, but is a mixture of guanajuatite with native bismuth and bismuthinite.

Among the rarer bismuth minerals may be included *lapalpite*, sulpho-telluride of bismuth and silver, found in the State of alisco, Mexico (*see* p. 43); *arsenobismite*, $2\text{BiO}_3 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, discovered in 1914, associated with barytes in the 600-foot level of the Mammoth mine, Tintic Mining District, Utah [3]; *nixite*, a basic copper-bismuth arsenate, also found in the Mammoth mine; *daubréeite*, a bismuth oxychloride; and *matildite*, another bismuth-silver mineral found at the Matilda mine, near Morococha, Peru (*see* p. 54).

Tetradymite is generally, but not exclusively, a primary mineral. It is present in many lode ores, especially those formed at shallow and moderate depths. Cosalite is of uncertain composition as analyses vary much; it is probably always primary [4].

Bismuth minerals are almost invariably associated with other ores in deposits, rarely occurring alone.

As the chloride and sulphate of bismuth are hydrolyzed in water, and even in dilute solutions, to insoluble compounds and the carbonate has a very low solubility, the metal is neither transported by cold mineral waters nor concentrated by processes of surface enrichment, remaining immobile in the oxidized zone [4]. Next to cinnabar, bismuthinite is of all the sulphide minerals the most insoluble in water.

Although bismuth forms trivalent, quadrivalent and quinivalent compounds, only trivalent compounds are found in nature. Arsenic, antimony and bismuth have chemically many points of similarity, but differ in others. Arsenic behaves usually as a non-metal or acid-forming element; antimony is both acid- and base-forming, whilst bismuth is

almost entirely a metal and base-forming. The native metals differ in that bismuth is almost invariably primary, whilst antimony and arsenic are secondary minerals. Antimony and bismuth are rarely associated in nature; arsenic and bismuth occasionally (*see* pp. 27, 31, 35, 36, 44).

OCCURRENCES OF BISMUTH

Bismuth deposits from their association with acid rocks rich in alkalis may be looked upon as being intermediary between those of the sulphides of molybdenum, copper and cobalt on the one hand, and those of tin, tungsten and uranium on the other. The latter are developed with deeper oxidation than the former. Bismuth is almost universally found in a quartz gangue.

Bismuth deposits may be roughly classified in three groups :

1. Those in which bismuth is associated with tin and copper, and with tungsten and molybdenum as accessories ;
2. Those in which bismuth is associated with cobalt and uranium ;
3. Those in which bismuth is associated with gold.

Bismuth-tin deposits.—These are developed especially in Bolivia, where a certain number of copper-tin lodes contain bismuth, with or without tungsten and tourmaline. On Chorolque Mountain, for example, the veins occur in quartz-trachyte or quartz-andesite, which in their vicinity has been considerably silicified. At Tasna the deposits are in slate cut by rhyolite dykes (*see* p. 49). The presence of copper and iron minerals in the ores from these mines makes the dressed ore metallurgically superior to those of Saxony (*see* p. 37).

Further examples of the occurrence of the bismuth-tin type of deposit are to be found in Chile, Peru, Argentina, New South Wales, Queensland, Tasmania, Cornwall and France (*see* pp. 22, 28, 33, 36) [5].

Bismuth-cobalt deposits.—These are typically exemplified at Schneeberg in Saxony (*see* p. 36), where a large number of narrow veins with quartz gangue occur in schists lying on granite. The veins form stockworks, which are rich at the surface, and in which some results of ancient faulting have

been proved. They have become quite unexploitable at a depth of about 1,400 ft., where they have left the schists and entered the granite below [5].

Bismuth-gold deposits.—The relatively frequent association of bismuth with gold illustrates the relations which exist between bismuth and the sulphur-arsenic-antimony group. Examples of such deposits are to be found in Queensland, New South Wales, Norway, the United States, etc. (*see* pp. 31, 38, 41, 44) [5].

As not a trace of bismuth has yet been found in the nickel matte derived from the smelting of Sudbury (Ontario) ores, it seems probable that the metal does not exist in magmatic deposits [6].

DRESSING OF BISMUTH ORES

As bismuth ores are usually associated in ore deposits with those of other metals, their dressing is sometimes a complicated procedure. Bismuth minerals, and those of most other metals such as tin, tungsten, molybdenum, silver and cobalt, in association with them, are many of them brittle, and it is difficult to prevent their being slimed prematurely, thereby making their subsequent separation more difficult. All kinds of concentrating tables for treating both coarse (sand) and fine (slime) products are in use, as well as flotation plants and magnetic separators.

As an example of the methods employed, the treatment of the tungsten-bismuth-molybdenum ore of the Burma-Queensland Corporation at Wolfram, Northern Queensland, will be briefly described :

The ore consists of the following minerals in a quartz gangue : Native bismuth, bismuthinite, bismutite, molybdenite and wolframite.

The pulp from the ore, milled in a stamp battery, is classified, the underflow being treated on Buss and Wilfley tables. A tungsten-bismuth concentrate is produced ; also a middling and a tailing. The tailing is sent to a flotation plant, and the middling is ground in pans. The pan product is classified, the overflow passing to a slime treatment plant, and the underflow being passed over Krupp and Isbell vanners. These

produce a second lot of tungsten-bismuth concentrate, a middling sent back to the Wilfley tables, and a tailing which is sent to the flotation plant. The material, consisting of various classifier overflows, and sent to the slime plant after being dewatered, is passed over slime tables. The tailing from these tables is returned to the flotation plant, the heads and middling being treated on buddles followed by Ludwig vanners, which produce a tungsten-bismuth concentrate.

The various concentrates produced by water-concentration are dried and screened to three products and an oversize, which is reground. The three products are separately treated by magnetic concentrators, and the resulting products are bismuth concentrate, tungsten concentrate and a tungsten-iron concentrate, from which an iron residue is eliminated on a Wilfley table.

The material, which is sent to the flotation plant and contains the bulk of the molybdenite, is settled, the resulting sludge being classified into different products, which are treated differentially with "kerosene liquor." Further details will be found in reference [7].

In one case a magnetic separator of the Ball-Norton type employed in Queensland for treating a magnetite-bismuth concentrate from the wet-dressing of the ore, raised the bismuth content from about 11 to 20%. Additional information on the magnetic separation of concentrate containing bismuth will be found in reference [8].

METALLURGY OF BISMUTH

Methods used for the reduction of bismuth from rich ore or concentrate are of two kinds, dry and wet.

Dry Methods

Dry methods are conducted either by liquation or by fusion.

The *liquation* or *melting* process was formerly used for rich ores containing native bismuth only. The ore was heated in inclined cylindrical retorts of different forms, the temperature being just enough to melt the bismuth, which, separated from the ore and trickling down the retorts, was tapped at the lower end and was caught in receptacles outside. The process was

THEIR OCCURRENCE, CHARACTERS AND USES 7

wasteful, as 5 to 6% minimum, and sometimes even one-third, of the bismuth was still left in the residue, and had to be recovered by further treatment [9/p. 594].

The *fusion* or *smelting* process is carried out in reverberatory furnaces, when large quantities of ore have to be dealt with, or in crucibles, with small quantities. Shaft furnaces are not used on account of the corrosive action of molten bismuth upon the linings. This process is more successful than the liquation process, as it permits the use of reducing agents to decompose any oxidized or sulphide ores.

When the ore is a sulphide, especially if it contains arsenic or antimony, it is usually first of all roasted, generally in a small reverberatory furnace with a long hearth. Bismuthinite, for example, by roasting is converted into bismuth oxide and sulphate, whilst arsenic and antimony if present are converted into trioxides. Part of these oxides is volatilized and a part is converted into arsenates and antimonates. Much of the arsenic and antimony in the latter is driven off by the addition of coke or charcoal towards the end of the roasting. Any volatilized oxide of bismuth is caught in condensers, connected with the flues.

As molten bismuth rapidly penetrates brickwork, the working hearth of a reverberatory furnace used for smelting is built on an iron pan. Crucibles, used for smelting bismuth ores, are made of fireclay only, or of fireclay with 10 to 20% plumbago added. They are heated in ordinary wind furnaces.

On account of the volatility of bismuth and of the oxide of bismuth, smelting must be conducted at a low temperature, and slags consequently must have a low melting-point and a low specific gravity, and be very fluid, so that the bismuth may easily settle. The fluxes used are soda ash with 10 to 30% lime and hæmatite. The lime helps to reduce the specific gravity of the slag, but its use is limited, as its silicates fuse at a high temperature. Only a small amount of hæmatite can be used, as although the iron silicates are very fluid their specific gravities are high. Fluorspar and pyrolusite are also used, the latter to replace hæmatite, as manganese silicates are very fluid. The reducing agent used with roasted ores is usually coal.

Native bismuth ores, which almost always contain some oxide and some bismuthinite, are usually smelted in crucibles, iron being added to the charge to decompose the bismuthinite, and charcoal, to reduce the oxide. As roasted ores often contain some sulphate as well as arsenates and antimonates iron is added to the charge.

Sulphide ores are sometimes smelted direct, without previous roasting, by the "precipitation" process. Iron is added to the charge, and decomposes bismuthinite, for example, by withdrawing its sulphur and forming sulphide of iron. The objection to the process is that the slags formed are very corrosive.

When copper and sulphur are present in a charge a matte is formed; with arsenic a speiss is formed, but some arsenic and copper will go into the bismuth.

In Bolivia the ores that are smelted there usually contain sulphides of bismuth, copper, iron, antimony and a little silver. They are usually roasted in reverberatory furnaces, and smelted afterwards in similar furnaces with about 3% coal, and lime, soda ash and fluorspar as fluxes. After complete fusion and settlement of a charge the lowest layer consists chiefly of metallic bismuth, and the next layers consist of bismuth-copper matte, which is worked up afterwards. The top layer consists of slag.

Wet Methods

Wet methods are used chiefly for the extraction of bismuth from metalliferous by-products containing bismuth, such as bismuthiferous litharge, anode sludge resulting from the electrolytic refining of lead and copper ores, etc. [2].

Bismuthiferous litharge is produced in the cupellation of argentiferous lead. Litharge free from bismuth is first formed; then the bismuth itself is oxidized and enters the litharge, the remainder of the bismuth remaining in the silver. The litharge is usually too poor to treat direct chemically, and is reduced to lead with charcoal or coke in a small blast furnace. The resulting bismuthiferous lead is cupelled; the first portion of litharge formed contains little bismuth, and is kept separate; later on the bismuth is oxidized and enters the litharge. If

this contains not less than 20% bismuth it is ground fine, and is treated in steam-heated stoneware jars with 15% hydrochloric acid. Lead chloride (PbCl_2) and bismuth trichloride (BiCl_3) are formed, a small portion of the former and all the latter being in solution. The solution is filtered off, is neutralized with soda ash, and bismuth oxychloride (BiOCl) is precipitated by adding water. The oxychloride, after being washed with hot water to remove any lead chloride, is dried and is reduced to metal by fusion in an iron crucible with carbon as a reducing agent, and glass, soda ash and lime, as fluxes.

This acid process could be applied to the treatment of oxide ores, but this is rarely done in practice [9/p. 596].

REFINING OF CRUDE BISMUTH

Crude bismuth is generally contaminated with arsenic, sulphur, iron, nickel, cobalt and antimony, and sometimes with gold, silver, lead, copper, sulphur, thallium and tellurium (*see* analyses, p. 11), so that it is not suitable for many purposes and must be refined.

Dry Methods

The general method of purification of bismuth that is used when the metal is wanted for alloying purposes is to melt it in crucibles with certain refining agents; the details vary somewhat, as is shown below.

Antimony is removed by Matthey's method by heating the bismuth up to the oxidation point of the antimony, and then by "poling" it with wood. The scum which forms, containing the antimony, is skimmed off as produced, but some bismuth is lost with it. Sometimes antimony is entirely removed by melting the bismuth in crucibles with bismuth oxide in amount from $2\frac{1}{2}$ to 3 times that of the antimony present; the scum, containing the antimony as oxide, is removed. In other cases the bismuth is fused in crucibles with potassium and sodium carbonates and sulphur. The double sulphide of antimony and sodium, which rises, is skimmed off [9/p. 597].

Arsenic is a common constituent of crude bismuth, but in

very small amount. It is removed by Matthey's method, by heating the bismuth in air for a long time at 395°C ., when the arsenic is volatilized without loss of bismuth. Arsenic is also removed by fusion of the bismuth in pots under a cover of caustic soda and nitre: the arsenic is rapidly oxidized to sodium arsenate [9/p. 597].

Copper is removed by stirring bismuth sulphide into the molten bismuth after oxidizable metals have been removed. A matte containing cuprous sulphide rises to the surface and is skimmed off [10].

Iron is eliminated from bismuth by fusion with nitre and common salt [9/p. 597].

Lead is removed, but generally not completely, by heating the bismuth in a current of air. The litharge formed also tends to oxidize other impurities. The slag or scoria, which is formed is skimmed off. In the case of much lead being present the crude bismuth is fused in cast-iron pots with bismuth oxychloride under a cover of potassium and sodium chlorides. The charge is well stirred with an iron stirrer, but a little iron enters the bismuth [9/p. 597]. Sometimes lead is removed from molten bismuth in Pattinson pots. The bismuth-lead alloy remains molten, whilst the rest of the bismuth forms crystals, which are removed [10].

Gold and *Silver* are removed in the crusts which are formed on the surface of the molten metal by the addition of 2% zinc [9/p. 597].

In the liquation method of refining, the bismuth is slowly melted and then allowed to solidify, when a large number of globules of pure bismuth will exude from the balance of the bismuth alloy containing the impurities, unless lead or silver be present. When this operation is performed on a sloping hearth of peculiar construction the purified molten bismuth falls away from the remainder [2].

Wet Methods

When bismuth of extreme purity, as for certain pharmaceutical preparations, is required, the crude metal is dissolved in nitric acid, and water is added. The precipitated sub-nitrate is filtered off and then boiled with an alkali to remove

THEIR OCCURRENCE, CHARACTERS AND USES 11

any remaining lead and arsenic. The sub-nitrate is used as a basis for making other salts of bismuth [2].

Further details of refining bismuth will be found in reference [11].

Up to the beginning of the Great War most of the bismuth compounds required for industrial purposes were prepared at Schneeberg in Saxony, but since then nearly all the Bolivian and Australian concentrates that have been produced, constituting the bulk of the world's supply, have been treated, and the resulting metal refined, in England [11].

Analyses of various samples of bismuth are given in the following table :

Analyses of Crude and Refined Bismuth

	Peruvian (crude).	Australian (crude).	"A commercial grade" (refined).	Bolivian (refined).	Saxon (refined).	Bohemian (refined).
	[9].	[9].	[12].	[13].	[10].	[10].
Bismuth	93.372	94.103	99.923	99.050	99.770	99.32
Silver	—	—	0.050	—	0.050	nil
Lead	—	—	0.005	—	nil	0.30
Copper	2.058	1.944	0.007	0.260	0.080	trace
Iron	—	—	0.005	—	trace	trace
Zinc	—	—	0.010	—	—	—
Antimony	4.570	2.621	—	0.560	—	—
Arsenic	nil	0.290	—	—	—	—

PROPERTIES OF BISMUTH

Bismuth is a greyish-white metal with a bright metallic lustre and a characteristic faint reddish tinge. It resembles antimony in appearance, but differs from it in having a foliated texture. It is a hard metal, but is so brittle that it can easily be powdered ; it therefore has neither ductility nor malleability.

The melting-point of pure bismuth is $271^{\circ}\text{C}.$, but that of ordinary commercial bismuth is about $264^{\circ}\text{C}.$ *In vacuo* it vaporizes at $292^{\circ}\text{C}.$, but in hydrogen at atmospheric pressure it commences to distil at $1,100^{\circ}\text{C}.$, boiling at temperatures up to $1,450^{\circ}\text{C}.$

The specific gravity of bismuth when molten is 10.055, and when solid, 9.82, so that it expands after solidification by about 2.3% of its volume. The molten metal can be cooled

6° C. below its solidifying-point and still remain liquid, but a rise of temperature occurs when it solidifies. When the metal is melted and allowed to cool till its surface begins to solidify and a crust is formed, if the rest of the metal is poured out fine large crystals are obtained.

Compared with silver ($= 100$) in each case the electrical conductivity of bismuth is 1.3 and its heat conductivity is 1.8, which are the lowest amongst those of the metals.

The atomic weight of bismuth is 208.0 and its specific heat 0.0305. The coefficient of expansion of bismuth by heat between 0° and 100° C. is 0.001341 of its length at 0° C.

Bismuth is the most diamagnetic substance known, *i.e.* in possession of the power of being repelled by a magnet. Antimony also possesses this property, but in a lesser degree. The two metals are used in forming the couples of a delicate thermopile, which is used in detecting very small changes of temperature.

The electrical resistance of bismuth increases when the metal is subjected to the action of a magnetic field, and again diminishes to normal when it is removed from the action of the field. Advantage is taken of this property of bismuth in the construction of instruments used for determining the strength of magnetic fields, *i.e.* in air gaps in dynamo electric machinery.

On exposure to ordinary air at normal temperature bismuth slightly oxidizes or becomes tarnished superficially with bismuthous oxide (Bi_2O_3). At a red heat in air it burns with a bluish flame, forming "flowers of bismuth" (Bi_2O_3). At a red heat it decomposes steam, but in air-free cold water there is no action.

Bismuth combines directly with chlorine, bromine and iodine. It dissolves in aqua regia or nitric acid, or in hot sulphuric acid forming the nitrate $\text{Bi}_2(\text{NO}_3)_3$, or the sulphate $\text{Bi}_2(\text{SO}_4)_3$, respectively. Hydrochloric acid has a little action on the metal, but only when hot. Hydrous basic salts, usually known as sub- or oxy-salts, are formed by the addition of water. The oxychloride is a dazzling white powder. The sulphide, Bi_2S_3 , is absorbed by molten bismuth in all proportions; at a high temperature the sulphur is volatilized almost completely.

THEIR OCCURRENCE, CHARACTERS AND USES 13

Bismuth forms compounds with arsenic and phosphorus, which are decomposed with increased heating. When treated with sodium-ammonium bismuth yields a bluish-black mass, which takes fire in air and decomposes water. By calcining 20 parts of bismuth with 16 of cream of tartar a silver-white potassium bismuth alloy with lamellar fracture is obtained.

The presence of bismuth in metals makes them brittle, and reduces their electrical conductivity. In the case of copper to be used for electrical work the limiting amount permitted is 0.005% bismuth; in the case of copper intended for brass-making the limit is raised to 0.01% bismuth. The amount of 0.04% bismuth is harmful in lead used for lining the chambers used in the making of sulphuric acid: 0.02% bismuth in lead used for making white lead makes it "common," the product acquiring a grey tint. The presence of only one part of bismuth in 8,000 of gold renders it unworkable. In ordinary alloy work the presence of arsenic neutralizes the bad effects of bismuth to some extent [2][9/p. 597][11][13].

USES OF BISMUTH

The chief uses of bismuth are for medicinal, surgical and toilet purposes; in making fusible alloys, electrical fuses, etc.; and for pigments used in the painting of porcelain and allied purposes. Its use in instruments for determining the strength of magnetic fields has been mentioned above.

The various salts used in medicine and for surgical operations are the sub-nitrate, the oxycarbonate, the oxychloride, the sub-salicylate, the sub-gallate and the sub-lactate.

Bismuth salts are used in medicine, chiefly for alleviating indigestion. The oxycarbonate is the salt principally used, and in a lesser degree the sub-nitrate; the former is the more easily swallowed. In surgery some bismuth salts are used for dressing wounds; some, including the sub-nitrate and the oxychloride, are administered before an operation. The patient is given a "bismuth meal," containing about 4 oz. of the salt, which is swallowed. The bismuth becoming distributed throughout the alimentary canal, an X-Ray photograph can be taken, in which defects in the digestive tracts are clearly outlined.

For toilet purposes the oxychloride and sub-nitrate were formerly much used ; latterly the cheaper oxide of zinc has been substituted.

The oxide of bismuth (Bi_2O_3) has been used as one of the constituents of optical glass ; in the staining of glass it acts by preventing the formation of colour by various substances which otherwise would be useful fluxes ; it is also used in the colouring of porcelain. The addition of 5% gold to the oxide gives a good copper-red glaze mixture, which has also the property of producing a golden lustre by reflected light. With less gold various blue and violet shades may be produced by altering the proportions. The sub-nitrate gives a colourless but iridescent glaze to porcelain, and, when mixed with chromic oxide, a yellowish glaze.

For gilding porcelain the oxide or sub-nitrate is used with 15 times its weight of gold. The mixture is applied with a brush and then fired.

Generally, in porcelain painting and enamelling, bismuth compounds are used as a flux chiefly to increase the fusibility of other colouring oxides such as those of manganese, chromium and copper.

Merinee's antimony yellow, a pigment with a good body and permanent, is a mixture of the sub-nitrate of bismuth and antimony tri-oxide (Sb_2O_3) [10] [12] [13 p. 639].

Owing to its brittleness metallic bismuth is very seldom used alone. A large number of bismuth alloys, principally those of low fusibility, are in use, and are described below. Bismuth amalgam, with or without the addition of lead and tin, is used for the silvering of mirrors. Fusible alloys are used in automatic sprinklers and other apparatus for fire prevention ; for safety plugs in boilers ; in dentistry for the making of dies from fresh plaster impressions ; for the setting of crystals in the detectors of radiophone receiving sets, and for many other purposes. Many fusible alloys melt in hot water.

Inflammable materials, such as tar, creosote, asphalt and non-drying oils, used for the waterproofing of cloth, wood, paper, etc., are rendered fireproof by the addition of 5 to 20% bismuth trichloride, with or without organic solvents (amyl acetate, etc.) [14].

THEIR OCCURRENCE, CHARACTERS AND USES 15

Enamels for cast iron, containing bismuth as a substitute for lead, can be prepared according to English patent No. 22,345 of 1899 with the following mixtures : Quartz, 10 to 30 ; boric acid or borax, 10 to 60 ; potash or saltpetre, 5 to 40 ; bismuth oxide, 20 to 80 ; and lithium compounds 5 to 30 parts [15].

ALLOYS OF BISMUTH

The general effect of adding bismuth to other metals is to increase the hardness and to lower the melting point, hence bismuth is very largely used in the composition of fusible alloys, some of which are liquid at as low a temperature as that of the human body. A very large number of alloys containing bismuth have been made and are in use. Heine [16] has made a list of 95 known fusible alloys containing different proportions of bismuth, tin, lead and cadmium and melting between 55.5° C. and 173.8° C., but there are many others containing these and other metals.

Tin and Bismuth readily combine in all proportions. A very small amount of bismuth added to tin increases its hardness, sonorousness, lustre and fusibility. No large quantity of bismuth, however, which is easily oxidized and often contains arsenic, should be used in the tin employed for lining the insides of culinary vessels. Primary alloys of tin and bismuth melt at lower temperatures than either of these metals. According to Claudet, an alloy of 40 parts of tin to 1 of bismuth is perfectly ductile.

Melting points of various ordinary tin-bismuth alloys are given in the following table :

Formula.	Tin.	Bismuth.	Solidifying point °C.
	%	%	
Sn ₃ Bi ₁	45.73	54.27	143
Sn ₄ Bi	69.21	30.79	190
Sn ₅ Bi	52.91	47.09	160
Sn ₆ Bi ₁	27.25	72.75	170
SnBi ₁	21.93	78.07	190

[17].

Mercury added to alloys reduces their melting points still further. An alloy containing : Lead, 1 ; bismuth, 1 ; mercury,

3 parts, is liquid at ordinary temperatures. Fusible teaspoons, which melt in hot water, are made of : Bismuth, 8 ; tin, 3 ; lead, 5 ; and mercury, 1 to 2 parts [17].

Mercury and bismuth in different proportions form a large number of *amalgams*. Mercury, 2 parts, and bismuth, 1 part, form a pasty mass ; but mercury, 4 parts, and bismuth, 1 part, form a liquid alloy, which is used for the silvering of mirrors and the interiors of vacuum flasks. For the latter purpose the following alloys are also used :

Bismuth (parts)	1	1	1
Lead (")	1	1	1
Tin (")	1	1	1
Mercury (")	1	2	9

[19/p. 531].

D'Arcet's mercuric metal, which melts at 45° C., is used for taking casts of anatomical specimens, making a perfect impression on moulding. It consists of : Bismuth, 2 ; lead, 1 ; tin, 1 ; mercury, 5 parts.

Antimony and Bismuth binary alloys all expand on solidification. The alloy with equal parts has a greater expansion than any other known metal or alloy. Antimony is used in a number of ternary and more complex bismuth alloys, some of which are given in the following table :

Complex Alloys of Bismuth and Antimony

	Bismuth.	Lead.	Tin.	Zinc.	Copper.	Antimony.
	$\frac{w}{\%}$	$\frac{w}{\%}$	$\frac{w}{\%}$	$\frac{w}{\%}$	$\frac{w}{\%}$	$\frac{w}{\%}$
Britannia Metal . .	2	—	90	—	2	6
" " . .	5	—	85	1.5	3.5	5
" " . .	8	8.5	75	—	—	8.5
Cliché Metal III . .	9	32.5	48	—	—	10.5
Karmarsch . .	1.6	—	85	1.4	3.6	5
A pewter . .	1.8	—	89.3	—	1.8	7.2
Trabuck Metal ¹ . .	2	—	87.5	—	—	5
Type Metal . .	22.23	50	—	—	—	27.77
" " (German) . .	29.58	65.1	—	—	—	5.82
Stercotype Metal . .	15	70	—	—	—	15

¹ + 5.5% nickel.

[17] [18].

Cliché metal is used in automatic water sprinklers and is especially suitable for "dabbing" rollers used in printing cotton goods.

THEIR OCCURRENCE, CHARACTERS AND USES 17

For filling defective places in metallic castings an alloy of bismuth, 1; antimony, 3; and lead, 8 parts, may be used [19].

Copper, when alloyed with bismuth in the proportion of 1 to 2, makes an alloy which expands considerably on solidification. A red crystalline alloy results from mixing 1 part of copper with 4 of bismuth. *Bismuth bronzes* used for making spoons, jugs, teapots, etc., are made from a number of metals. They are unoxidizable, keep a good colour, and are easily polished. The following are examples of the composition of such bronzes :

Bismuth Bronzes

No.	1.	2.	3.
	$\frac{0.7}{10}$	$\frac{0.7}{10}$	$\frac{0.7}{10}$
Copper	25	69	45
Nickel	24	10	32.5
Antimony	50	15	—
Bismuth	1	1	1
Zinc	—	4	5.5
Aluminium	—	1	—
Tin	—	—	16

No. 3, a sheathing bronze, ¹ withstands sea-water. [10] [18].

Guillaume's Metal is a binary alloy containing bismuth, 37.7%; copper, 64.3%. *Neogen* contains: Bismuth, 0.5%; tin, 2%; zinc, 27%; copper, 58%; nickel, 12%; aluminium, 0.5% [18].

Cadmium acts like bismuth in lowering the melting point of many alloys, but it has the advantage of not producing as much brittleness as bismuth. The following tables give compositions of a number of bismuth-cadmium alloys :

Bismuth-Cadmium Alloys (1)

No.	1	2	3	4	5	6	7	8	9	10	11 ¹
Melting Point °C.	95	95	95	82	77	75	71	70	65	60	—
Bismuth (parts)	3	5	2	7	8	8	5	7	8	7½	8
Cadmium „	1	1	1	1	1	10	2	1	1	2	2½
Lead „	—	—	—	4	0	8	4	4	5	4	3
Tin „	2	3	3	4	1½	3	2	2	2	2	3

¹ Guthrie's eutectic.

Bismuth-Cadmium Alloys (2)

	Melting point °C.	Bismuth.	Cadmium.	Lead.	Tin.
		%	%	%	%
A fusible metal .	80	35.3	9.5	35.1	20
" " "	75	27.0	34.5	27.6	10.3
" " "	70	50.0	7.1	28.6	14.3
Lipowitz's alloy.	60	50.0	10.6	26.7	13.3
Wood's alloy.	70	50.0	12.5	25.0	12.5

[18].

Lipowitz's alloy is of a silver-white colour and lustre ; it can be bent short, hammered and turned, and is well adapted for casting delicate objects, which may not be strongly heated and are a white colour [17]. Wood's alloy is used for soldering in hot water, and for setting crystals in wireless rectifying apparatus.

The compositions of some solders containing bismuth are given in the following table :

Solders containing Bismuth

	Melting point °C.	Bismuth.	Lead.	Tin.
No. 1 (parts)	94	3	3	5
" 2 " " " "	113	2	2	1
" 3 " " " " " "	144	1	2	2
" 4 " " " " " "	154	1	3	3
" 5 " " " " " "	160	1	4	4
Pewterer's solder (parts)	—	2	4	3
Aluminium " (" ")	—	5	(zinc) 30	65

[18].

The compositions and melting points of a series of alloys, containing bismuth, and used in the tempering of steel tools, are given in the following table :

Steel Tempering Alloys

Melting point °C.	100	108	118	122	130	132	143	151	154	160	165	171	177
Bismuth (parts) .	8	8	8	8	8	8	8	8	8	8	8	8	8
Lead (parts)	6	8	8	8	10	12	16	16	24	26	28	30	32
Tin "	3	3	6	8	8	8	14	16	24	24	24	24	24

[10].

THEIR OCCURRENCE, CHARACTERS AND USES 19

Details of a few of the many other bismuth alloys not mentioned above are given in the following table :

Various Bismuth Alloys

	Melting point °C.	Bismuth.	Lead.	Tin.
		%	%	%
A fusible metal	91·6	50	33·5	16·5
" " " "	84·5	50	31·25	18·75
" " " "	68·5	52·2	26	14·8
D'Arcet's metal	93·7	50	25	25
Newton's ¹ " " " "	94·4	50	31·25	18·75
Rose's ¹ " " " "	100	50	28	22
Warne's " " " "	—	26	—	37 ²
Onion's alloy	92	50	30	20
For delicate castings I	—	50	25	25
" " II	—	27·3	59·1	13·1

[18].

¹ Formerly similar alloys but of higher melting point were used in the making of the so-called safety plates inserted in the tops of steam boilers. In practice it was found that oxidation and other causes interfered with their efficiency.

² + 26% nickel and 11% cobalt.

A bismuth alloy for cementing glass consists of bismuth, 1 ; lead, 3 ; and tin, 2 parts : it is well adapted for fastening together the metal parts on glass lamps [19].

MARKETING AND PRICES OF BISMUTH

Refined bismuth is usually put on the market in 25-lb. bars, which are packed in wooden boxes, holding 150 lb., with wooden wedges between the bars, the minimum wholesale lot being 500 lb. There are no standard specifications, but the refined metal must be 99·9% pure. When used for making medicines the metal must be absolutely free from arsenic : for alloy-making the freedom from arsenic is not so important [12].

The sale of refined bismuth is largely under the control of the Bismuth Association, a group of refiners in England, working with, and under the direction of, Messrs. Johnson, Matthey and Co. Ltd., London. The Association commands the market in Europe, and the two American refining companies, the United States Smelting, Refining and Mining Co., and the American Smelting and Refining Co., working in co-ordination

with it, control the sale of bismuth in the United States. Selling prices of refined bismuth are fixed by the Association. London and New York are the two market centres.

Average annual prices in London for recent years are given in the following table :

Bismuth Prices in London

	1914.	1915.	1916.	1917.	1918.	1919.	1920.	1921.	1922.	1923.	1924.
Price per lb.	10/-	10/-	11/-	11/-	11/-	12/6	12/6	12/6	9/-	10/-	8/6

THE WORLD'S PRODUCTION OF BISMUTH

As the statistical publications of foreign countries do not usually give the metal contents of the various bismuth materials that are produced or exported, it is not possible to give exact figures of the world's production of bismuth. A summary of the information available is given in the table on page 21.

THEIR OCCURRENCE, CHARACTERS AND USES 21

(Metric tons)

Country.	Material.	Bismuth content, %	1915.	1916.	1917.	1918.	1919.	1920.	1921.	1922. ¹	1923.
Argentina ¹	Ore	—	—	18·00	275·70	25·00	—	—	—	—	—
Australia:											
New South Wales ²	Ore and metal	—	18·30	30·18	20·32	31·30	19·30	77·22	8·13	6·9	—
Northern Territory ³	Ore	—	—	—	—	0·06	—	—	—	—	—
Queensland ⁴	Ore and metal	—	2·58	3·61	4·06	21·00	2·03	0·97	0·03	—	0·25
" "	Tungsten-bismuth conc.	—	—	—	—	—	—	—	—	—	—
Tasmania ⁵	—	—	250·81	138·69	133·35	116·13	142·14	49·83	—	—	—
Western Australia ⁶	—	—	5·59	3·57	4·28	4·08	1·80	0·10	0·05	—	—
Austria ⁷	Ore	—	1·02	0·20	0·51	—	0·05	—	—	—	—
Bolivia ⁷	Ore and metal	—	602·40	325·00	—	—	—	—	—	—	—
" (exports)	Concentrate	25-35	474·83	446·54	58·25	75·57	38·59	27·01	4·71	—	—
" (exports)	Metal	85	—	—	255·24	248·98	109·45	194·54	—	134·0	—
" (exports)	Ore	5-30	181·50	168·10	111·06	111·52	93·83	133·01	23·94	—	—
" (exports)	Residue	20-50	6·24	53·79	160·14	54·00	72·51	63·18	—	167·0 ¹⁸	—
China ⁸ (exports)	Ore	—	—	—	—	—	86·30	90·42	116·89	—	—
Germany ⁹ (Saxony)	Bismuth conc.	10-12	46	3·75	49	113	66·30	31	27	—	—
" "	Tin-bismuth conc.	10-12	—	—	—	31	9	1	—	—	—
" "	Cobalt-nickel-bismuth conc.	10-12	151	118	133	150	122	131	134	—	—
India (British) ¹⁰	Metal	—	—	—	0·25	—	—	—	—	—	—
Japan ¹¹	Ore	—	3·50	0·30	0·44	0·73	0·35	0·22	0·74	2·6	—
" (exports)	Ore	—	6·35	0·79	1·23	0·88	0·43	—	—	—	—
Norway ¹² (exports)	Ore	—	10	9	—	—	—	—	—	—	—
Peru ¹³ (exports)	Metal	—	—	—	1·36	—	—	7·82	—	6·5	1·28
Rhodesia (Northern) ¹⁴	Ore and metal	—	0·37	—	0·55	—	1·22	—	—	—	—
Spain ¹⁵	Ore	16	16·95	10·86	13·90	33·59	75·00	53·30	54·00	48·00	91·0
Union of South Africa ¹⁶	Ore	—	—	—	—	—	0·39	—	—	—	—
United States ¹ (estimated)	Metal	—	—	—	—	—	145	114	147	—	—

¹ Mineral Industry, 1923. ² N. S. W. Ann. Repts., Dept. Mines. ³ N. Territory, Repts. Administrators for year ended June 30. ⁴ Queensland Under Sec. Mines Ann. Repts. ⁵ Tasmania, Ann. Repts. Sec. Mines. ⁶ W. Australia, Dept. Mines Ann. Repts. ⁷ U. S. Geol. Survey Min. Res., 1922, Pt. I, p. 18. ⁸ Imperial Mineral Resources Bureau. ⁹ From Sachsische Oberbergamt of Freiberg, Ger. Min. Cham. of Comm. in Germany (Inc.) ¹⁰ Repts. Geol. Surv. India, 49, p. 74. ¹¹ Min. Bureau Dept. Agric. and Comm., Tokyo. ¹² Per Norwegian Consul-General, London. ¹³ Rhodesia Cham. Mines ¹⁴ Ore, conc. and res. ¹⁵ Union of S. Africa, Dept. Mines and Indus. Ann. Repts. ¹⁶ Ann. Repts.

CHAPTER II

SOURCES OF SUPPLY OF BISMUTH ORES

(a) BRITISH EMPIRE

EUROPE

GREAT BRITAIN

England.—Bismuth minerals occur in unimportant amount in various places in Cornwall and Cumberland. In Cornwall bismuth was known at Pengreep, Gwennap, before 1775. Native bismuth was met with nearly 100 years ago embedded in red jasper in two of the copper lodes at Botallack, St. Just. Bismuth, usually native, has also been found at Herland, St. Ives Consols, East Pool, Pednandrea, Wheal Sparnon and Trethurgy mines, and at various places at St. Austell, St. Columb and Roche. In the Levant mine at St. Just, the copper lodes contain a variety of minerals, including native bismuth, bismuthinite and bismutite. The same bismuth minerals occurred in Wheal Owles, St. Just, the principal one, however, being bismutite, which was also the chief mineral at Wheal Coates, St. Agnes. In the old Fowey Consols mine in the parish of Tywardreath, bismuthinite was very plentiful and generally crystallized in the cavities which occurred in chalcopyrite. The copper ores of the Dolcoath mine at Redruth were in places associated with those of bismuth, cobalt, nickel and uranium.

In all, sales of about 5 tons of bismuth ores have been reported from mines in Cornwall [20][21][22][23].

In Cumberland some of the tungsten-bearing quartz veins of the Carrock mines, near Grainsgill, the most important of which is the Brandy Gill or Emerson's vein, contain a number of minerals, including native bismuth and auriferous tetradymite [24].

Scotland.—Native bismuth has been found at Alva, Stirling-shire.

There was formerly a very small production of bismuth ore in England, but of late years there has been none.

Recent exports and imports of bismuth ore and metal are given in the following table :

Trade of the United Kingdom in Bismuth¹

			1920.	1921.	1922.
Bismuth Ore .	Imports	Long tons	485.4	191.9	178.4
" " .	"	Value, £	106,875	37,071	26,996
" " .	Exports	Long tons	—	3.9	—
" " .	"	Value, £	—	1,123	—
" Metal .	Exports	Long tons	113.1	87.2	141.8
" " .	"	Value, £	157,276	76,166	111,859
" " .	Imports	Long tons	3.9	27.7	104.6
" " .	"	Value, £	—	14,406	94,221

¹ *Ann. Statement of Trade of United Kingdom, 1, 1922.*

ASIA

INDIA

The only part of India where bismuth ores are at all of common occurrence is the Tenasserim Division of Lower Burma, but even here ore extraction has been made only on a very small scale. In the Tavoy district native bismuth and bismuthinite are found in the tungsten-tin veins of some localities, *e.g.* Kanbauk, Kalonta, Zinba and Putletto. They are also found in similar veins in the neighbouring districts of Amherst and Mergui. The veins carry pyrite and molybdenite in addition to cassiterite, wolframite and the bismuth minerals. Occasionally other sulphides, *e.g.* pyrrhotite, chalcopyrite, galena and blende, are found. It is considered that the bismuth minerals originated in the granite in the same manner as the wolframite and cassiterite, but from the fact that bismuth is often found in thin filaments deposited on, or cutting through, the wolframite it belongs to a later period.

In the same districts of Burma are some eluvial deposits, which have been formed on hillsides by general denudation,

24 SOURCES OF SUPPLY OF BISMUTH ORES

and the consequent breaking-down of veins containing cassiterite, wolframite and bismuth minerals, these being collected on the surface soil. These deposits are often profitable to work by sluicing. The bismuth minerals are either hand-picked from the clean concentrates produced, or are recovered chemically from the tin product after magnetic separation of the wolframite. This latter treatment is not carried out in India, the concentrate usually being shipped to England for the purpose ; thus the total bismuth production is not known but it is almost insignificant. In the only recorded case 5 cwt. of bismuth concentrate shipped separately as such was worth £163.

In the copper ores of the Singhbhum district of the Province of Bihar and Orissa there are traces of bismuth [25] [26].

AFRICA

NORTHERN RHODESIA

Bismuth is widely distributed in Northern Rhodesia, the most promising area being the Kaomba field in the higher ground of the Luano Valley, about 100 miles east of Broken Hill and 90 miles from the railway. The largest deposits are said to be those of the Tanganyika Concessions, on which no development has been done, but large parcels of ore have been sold from other claims.

The bismuth exists in the form of bismuthinite in fissure veins of pyritous quartz, which traverse chlorite schists. The veins are small, but one has been proved for a length of 500 ft. A small amount of bismuth ore has also been mined in the Susaka district.

Some bismuth deposits contain gold ; in fact almost all the present gold output of the country comes from mines in which gold is associated with bismuth.

The total production of bismuth ore in Northern Rhodesia to the end of 1921 was 6.2 tons, of value £3,491 [27] [28].

SOUTHERN RHODESIA

Ores of bismuth have been found in a number of places in Southern Rhodesia, principally in the Lomagundi, Umtali and

Victoria districts. Native bismuth, bismuthinite, bismuth ochre and bismutite have all been found, and although some development work has been done in the Lomagundi district, so far there has been no production of ore [29].

In the Umtali gold belt bismuthinite is an important constituent of a quartz vein, and bismutite occurs in the outcrops of several other reefs [30].

UNION OF SOUTH AFRICA

Bismuth has been found in some of the gold ores of the Sabi district, and in the Stavoren tin mine, Transvaal. In 1897, several tons of rich bismutite ore were mined on the farm Geweerfontein in the Bushveld Granite Area from one of the pipe-like deposits found in the area. Some recent work on the deposit gave indifferent results [30A].

In the Glynn's Reef in the Lydenberg district of the Transvaal a little bismuth is associated with the gold in the ore.

NORTH AMERICA

CANADA

British Columbia.—In the Rossland district of British Columbia bismuthinite is found with chalcopyrite, pyrrhotite, arsenopyrite and molybdenite in the gold-copper-silver deposits of the locality. These are steeply-dipping replacement veins along shear zones in monzonite and augite-porphyry, and are deep-seated in origin. The gangue minerals include quartz, magnetite, calcite and biotite [31/p. 698].

Ontario.—Native bismuth occurs in almost all the veins of the Cobalt district of the Temiskaming Division of Ontario, which are described in the Imperial Institute monograph, *Silver Ores* (1921, p. 44). Sometimes antimony is present with the bismuth as well.

In the South Lorrain Silver Area, native silver is in one place associated with smaltite, chalcopyrite, chloanthite and native bismuth in a calcite gangue [32/p. 143].

In the Otter Township, near the north shore of Lake Huron, a quartz vein with some calcite in quartz dolerite (diabase) carries small masses of cobaltite and native bismuth. One

26 SOURCES OF SUPPLY OF BISMUTH ORES

sample, consisting mostly of bismuth, gave on assay : Gold, 0.3 oz. ; silver, 15.9 oz. per ton ; bismuth, 59.5% ; cobalt, trace. Another vein consists of quartz having a comb structure. Calcite and occasionally cobaltite and native bismuth have been deposited between the quartz layers, and thin sheets of bismuth sometimes occur on the smooth faces of the quartz crystals [32/p. 196].

In the Shining Tree Silver Area, according to R. B. Stewart, much bloom, with smaltite, chalcopyrite and a small amount of bismuth was observed in several of the veins near Fournier Lake [32/p. 190].

Native bismuth occurs in the Port Arthur veins, Lake Superior Silver district, 500 miles west of Cobalt [32/p. 203].

AUSTRALASIA

AUSTRALIA

In Australia native bismuth and other bismuth minerals are found associated in a remarkable manner with those of molybdenum, tin and tungsten, and generally also with fluor-spar, pyrite, chalcopyrite and apatite in a number of pipes, which occur in granitic rocks in Queensland and New South Wales, and which have been fully described in the Imperial Institute monographs, *Tin Ores* (1919) ; *Tungsten Ores* (1920), and *Molybdenum Ores* (1922). The rich ore is usually patchy and is seldom found below a depth of 100 ft. Bismuth has been found also in Tasmania, South Australia, Victoria and Western Australia, but generally only in very small amounts.

New South Wales.—Bismuth deposits occur in New South Wales principally in the New England district, in the N.E. ; in the Cobar district, in the north-central part ; and in the Whipstick district, in the S.E. of the State.

In the New England district the most important deposits are in the neighbourhood of Kingsgate, which is about 20 miles east of Glen Innes. The deposits are near and not more than 400 yds. from the contact between granite and altered slates, and consist of pipe veins or oval masses of quartz of

varying thickness, which go down in the granite generally vertically. At surface the bismuth minerals consist of the oxide, the carbonate and sometimes native bismuth: at depth, of native bismuth and bismuthinite. The gangue mineral is mainly quartz.

In addition to the bismuth minerals, molybdenite, cassiterite and arsenopyrite are also found, if not immediately associated with these minerals, then not far away in the same area.

To the north of Glen Innes bismuth is found in association with cassiterite in irregular quartz veins. The ore-bodies traverse a fine-grained micaceous felsitic rock, which is surrounded by altered sedimentary rocks. They sometimes form networks of veins, and at other times masses of quartz, one of which at the surface was 40 ft. by 20 ft. in area. Molybdenite, wolframite and arsenopyrite are associated minerals [32/p. 257].

Bismuth has been found at many other places in the New England district, including Silent Grove parish, where native bismuth, bismuthinite and cassiterite are found in veins.

In the S.E. portion of the State are also to be found irregular cylindrical pipes in granite containing bismuth ores, the gangue minerals being coarse feldspar, quartz, mica, and, in small quantity, garnet. At surface the ores are usually bismuth ochre and bismutite, but at depth, bismuthinite. There are also large masses of white quartz containing native bismuth. The Whipstick area in which the principal deposits occur is midway between Pambula and Bombala. The most important deposits are at Jingera, but there are many others, including those at Adelong and Captain's Flat. In the Jingera ore-bodies, which consist of pipes or lodes, there are, in association with those of bismuth, ores of silver and manganese as well as molybdenite, occurring in a felspathic matrix, the country being coarse mica-granite [10].

Rich deposits of bismuth, tungsten and molybdenum minerals in quartz reefs 3 to 4½ ft. wide were discovered in the Jingera Mts. in 1917.

Bismuthinite is found in small quantity in association with chalcopyrite and pyrrhotite in certain of the replacement veins of the Great Cobar mine, no longer worked, in Co.

28 SOURCES OF SUPPLY OF BISMUTH ORES

Robinson, which are lenticular, from 10 to 120 ft. in width, and have been mined to a depth of 1,600 ft. The veins are found in 'deeply eroded desert country of ancient Palæozoic sedimentary rocks—sandstone and slate—which they cut in strike and dip at acute angles. The bismuth content sometimes amounts to 2%. The gangue mineral is quartz, in which an iron silicate, *ekmannite*, is present. Bismuth is also associated with copper ore in other parts of the State.

For descriptions of occurrences of bismuth and tungsten in pegmatite veins in Northern New South Wales, see [34].

Queensland.—Bismuth minerals have been found in about seventy different localities in Queensland, and have been recovered in most cases as a by-product, principally in the treatment of tungsten, tin and molybdenum ores. Descriptions of many of the deposits of such ores are given in the Imperial Institute monographs mentioned above (p. 26). In some cases bismuth is won from bismuth-gold deposits, when it is generally the primary metal. Deposits containing bismuth are situated almost entirely in the eastern districts of the State, of which Cook and Burnett are the most important. There are about thirty occurrences in the former and about a dozen in the latter. Burnett Co. has produced about two-thirds of the entire bismuth output of Queensland.

The commonest bismuth minerals met with are native bismuth, bismutite, bismuthinite and bismuth ochre; tetradymite and its variety, joseite, are occasionally found.

Metallic minerals found in association with bismuth are gold, silver, wolframite, molybdenite, cassiterite, pyrolusite, malchite, chalcopyrite and other copper ores, blende, galena and iron ores. Common gangues include quartz (the commonest), calcite, chlorite, fluorspar, epidote, felspar, slate, etc.

Alluvial deposits containing native bismuth and bismuthinite in association with gold, silver, garnets, etc., are found in a few places [35].

There are four distinct types of deposits in Queensland in which bismuth ores occur :

1. The commonest and most numerous, but not the most productive, in which a formation of greisen and quartz occurs

in granite, or in altered sedimentary rocks close to granite. With these bismuth ochre is commonly a surface mineral.

2. The irregular magnetite mass associated with Permo-Carboniferous limestones at Mt. Biggenden (*see below*).

3. The volcanic breccia at Mt. Shamrock (*see below*) in which with associated diorite, felsite and mudstone, the bismuth ore forms irregular mineral impregnations and veins.

4. That at Eukalunda (*see below*) in which bismuth is present in defined copper lodes, the associated rock being of sedimentary origin and of Permo-Carboniferous age [10].

In *Cook District* in the granite, greisen-schist, quartz-porphyry and slate of the Chillagoe and Herberton fields (the latter extending into Kennedy North district) the bismuth deposits occur in defined lodes, irregular deposits, vugs or cavities, and impregnations, usually as native bismuth, bismuthinite, bismuth ochre and bismutite. Wolframite and molybdenite are the common associated minerals, but ores of copper, zinc, lead, iron, manganese and tin are found in places. The deposits have been mined mainly on account of their molybdenite and wolframite contents, in which native bismuth exists in the form of filaments in the cleavages of the molybdenite, greatly lessening the value of that mineral by its presence [10].

Occurrences of bismuth are most numerous in Hodgkinson and Lynd counties, but there are other deposits in Nares, Victor, Tate and Bolwarra counties.

In Hodgkinson Co. bismuth ochre and bismutite are the commonest bismuth minerals in some parts; bismuthinite in others. At Stannary Hills molybdenite and wolframite are the principal associated minerals. At Wolfram Camp, molybdenite, wolframite, scheelite, cassiterite, arsenopyrite and pyrolusite are associated with bismuth ores.

In Lynd Co. native bismuth and bismutite are the commonest ores. Wolframite is almost invariably present either with molybdenite or cassiterite. The principal deposits are at Fisherton on the Tate River; at the Wolfram mine at Lappa Lappa; at Emuford, and in the Bamfort mines. The last are the most important in the district, and contain wolframite, scheelite, molybdenite and arsenopyrite. Very little of the bismuth was deposited with the molybdenite, most of it being

30 SOURCES OF SUPPLY OF BISMUTH ORES

distinctly younger than the crystalline quartz and quartzite, the small interstitial cavities of which are its home. The bismuth occurs native, as bismuthinite, bismutite and bismite (ochre). The bismuth minerals abound in the cellular quartzite as well as among the vug fillings. Only very rarely do they penetrate the accompanying minerals, and it is presumed therefore that bismuth was the last metal thrown down. Bismuthinite is sometimes interlaminated with molybdenite. Native bismuth is most common near the surface.

In the Dog mine, two flat-lying pipes of quartz, from 6 to 8 ft. in diameter, yielded wolframite, bismuth, molybdenite and much polar magnetite. In the Evening Star mine, the pipe consisted of bluish crystalline quartz with scattered bunches of molybdenite, some pyrite and a little native bismuth and bismuthinite. The surrounding silicified greisen also carries a little molybdenite and bismuth. On the Ferguson United, one pipe, 5 ft. in diameter, carried wolframite with quite 4% bismuth, in the shallow ground. The mine has produced several tons of bismuth, besides wolframite and molybdenite. In the Haymaker mine, which is on Bamford Hill, the deposit consisted of a tabular mass from 5 to 7 ft. in thickness and 60 ft. wide; it has been followed 120 ft. on the dip at angles from 45° to 70°. Branch pipes drop off from this tabular mass. The lode material consists of bluish quartzite, through which run contorted shoots of wolframite and bismuth. One portion of No. 5 pipe contained bismuth only (native and carbonate) [35].

At Victor Creek on the Percy River in Victor Co. is alluvial material containing bismutite.

In *Kennedy North District* are several deposits in which native bismuth is the common ore mineral. In the Great Britain mine at Colgarra, in Cardwell Co. bismuthinite is associated with galena and blende.

The Glen bismuth mines between Herberton and Mt. Garnet have been described by W. C. W. Pearce [36]. The veins or lodes in biotite-granite are horizontal, and appear to occupy greisenized portions of the granite. The thickness varies from 9 to 12 in., and the filling consists of topaz (gangue), bismutite, specks of native bismuth and wolframite.

The ore was hand-picked, jigged and re-jigged until a clean concentrate was obtained for the market. Bagged concentrate gave from 25 to 30% bismuth and from 30 to 35% tungstic acid.

In *Kennedy South District* are several bismuth occurrences in Sellheim Co. In the Daisy Bell mine native bismuth, bismuth ochre, bismutite and bismuthinite are associated with native gold, pyrolusite, chalcopyrite and other copper minerals. At Eukalunda Bismuth mine native bismuth occurs with chalcopyrite and pyrolusite. Bismuth mining was formerly of importance here.

In *Port Curtis District* native bismuth and bismutite are found in Flinders Co. with molybdenite, wolframite, tungstic ochre and wad.

In *Burnett District*, in Cook Co., are important deposits at Biggenden, Mt. Shamrock, Mt. Havilah and at Mt. Steadman. Bismuthinite is the commonest ore, but native bismuth, bismuth ochre and bismutite also occur. The ores are associated with native gold, and sometimes also with native silver [35]. At Biggenden native bismuth is the ore of primary value, native gold, which is also present, being of secondary value. Other bismuth minerals are present, as well as the associated minerals, pyrite, arsenopyrite, calcite, muscovite, and epidote. No well-defined mineral belts or zones have been discovered so far in the deposits. The magnetite matrix appears to be an old intrusive rock, and is closely associated with diorite, greenish shales, tuffs, sandstones and fossiliferous limestones, these sedimentary rocks being a N.-W. extension of those of the Gympie goldfield [10].

At Mt. Shamrock, native bismuth is found with *bismuthaurite*, a native bismuth-gold invariably fine-grained, but otherwise having all the properties of native bismuth, and the telluride of bismuth, joseite, together with native gold, arsenopyrite and pyrite, all closely associated. The minerals are present generally in veinlets crossing mudstone and diorite, or as irregular patches and pockets in felsite, or as irregular and concentric coverings to the fragments in a volcanic breccia made up of mudstone, felsite and diorite. Occasionally small isolated nodules of native bismuth with as much as 1% gold

32 SOURCES OF SUPPLY OF BISMUTH ORES

are found in the breccia and in the felsite matrix. Joseite is found in irregular masses, rich both in bismuth and gold. Its bismuth content at Mt. Shamrock is sometimes as high as 90% owing probably to admixture of metallic bismuth; the usual percentage is 80. Gold is the principal product, but little is recovered free from bismuth. The gold-bismuth product was before the war sent to Germany, as it was not acceptable to English buyers. The gold was valued at £3 per ounce only, so that, for example, with a ton of concentrate containing 50 oz. gold the deduction on the gold alone was about £50 [10].

In the *Moreton, Burke, Darling Downs, Leichardt* and *Wide Bay* districts are a number of deposits in nearly all of which bismuth ores are associated with native gold and, often, native silver. In Pumpkin Gully, in Beaconsfield Co. of Burke District, there is an alluvial gold deposit containing native bismuth, and this mineral is also found in an alluvial tin deposit at Stanthorpe, in Benetinct Co., Darling Downs District. At the Kabonga mine in the Kilkivan goldfield in Lennox Co., Wide Bay District, bismuthinite occurs with native gold, magnetite, pyrite, chalcopyrite and other copper minerals in a quartz matrix [35].

South Australia.—Various bismuth minerals have been found at about twenty places in South Australia, and there was a production of bismuth ore between 1864 and 1876, inclusive, of 441 tons of value £18,031. The most important deposit was in the Balhanna Copper and Bismuth mine, in the Onkaparinga Hundred, worked from 1867 to 1876, which contained a remarkable number of minerals, including bismuthinite, native bismuth, bismutite, gold, silver, native copper, malachite, chalcopyrite and pyrite. The veinstones were quartz and calcite principally. Cobalt and manganese minerals, as well as graphite, were also found in the mine [37].

Tasmania.—Bismuth ores occur at a few places in Tasmania, and there has been a small output of bismuth, mostly as a by-product, but production ceased after 1921.

The principal mine formerly producing bismuth in a bismuth-tungsten-tin concentrate is the Shepherd and Murphy, at Moina in the Middlesex district. It is described in the Imperial Institute monographs, *Tin Ores* (1919, p. 68) and *Tungsten Ores* (1920, p. 41). Operations were carried on at a profit for eight years. Records showed that 24.88 tons of picked bismuth as bismuthinite were recovered from 55,586 tons of ore.

The All Nations mine, adjoining, was also a producer of bismuth-tungsten concentrate, which assayed: Bismuth as bismuthinite, 4%, and tungstic acid, 68%.

The Squib mine, in the same district, was formerly a producer of bismuth in the form of bismutite. Its lodes, containing tungsten, molybdenum and bismuth ore minerals, are partly in granite and partly in the adjacent quartzite; when in the granite the ores were richer. The bismuth product contains 40% metal [38] [39].

At Dundas, east of Zeehan, bismuthinite has been mined; it is associated here with pyrite and tetrahedrite.

Bismuthinite is found in tin mines at South Heemskirk, west of Zeehan.

Native bismuth and bismuthinite associated with wolframite occur in amphibolite at Mt. Ramsay about 25 miles N.N.E. of Zeehan.

The copper ores of Mt. Lyell contain bismuth, which is collected in the blister copper produced, from which it is subsequently eliminated in the electrolytic slime.

On King Island native bismuth occurs in one part of the scheelite deposit, also described in *Tungsten Ores* (p. 41) [40].

Victoria.—Native bismuth, bismuthinite and bismutite have been found at Linton, S.W. of Ballarat, Victoria, in association with copper ores, pyrite, molybdenite and wolframite.

The well-defined compound of bismuth and gold, maldonite, was first discovered in the quartz of Nuggety Reef at Maldon.

34 SOURCES OF SUPPLY OF BISMUTH ORES

Western Australia.—Bismutite has been found in pipes with scheelite at Melville in Western Australia, but owing to limited market demands mining operations have been restricted [41].

NEW ZEALAND

The only recorded occurrence of bismuth in New Zealand was, according to Skey, in the Owen Goldfield, where native bismuth was found in gold ores [42].

CHAPTER III

SOURCES OF SUPPLY OF BISMUTH ORES—*continued*

(b) FOREIGN COUNTRIES

EUROPE

AUSTRIA

FAHLBANDS in gneiss- and mica-schists occur at Schladming in Styria, where they are known as *Branden* on account of the brown weathered zone they form at the surface. They are intersected by vertical quartz lodes, near which, and within the fahlbands, are nickel ores in the form of nests and nodules, in which are also native bismuth and arsenic.

In the siderite deposits in schistose rocks in the Lölling-Hüttenberg district of Carinthia, native bismuth is found with löllingite (FeAs_2), ankerite, pyrite and barytes [6/pp. 822 and 949].

CZECHOSLOVAKIA

Native bismuth, bismuthinite, and bismuth ochre are found in association with silver, cobalt and uranium ores at Joachimstal, Bohemia. The deposits are described in the Imperial Institute monograph, *Cobalt Ores* (1924, p. 34).

FRANCE

At Meymac in the Department of Corrèze, France, is a small deposit of tin-tungsten ores. The deposit, a quartz lode, is to the south of a granulitic chain in porphyry-granite, with black mica and large felspar crystals, sprinkled with muscovite and enclosing everywhere nests of radiating tourmaline, and crossed at numerous points by dykes of saccharoidal granulite and pegmatite. The quartz lode in this granite is sometimes several metres in thickness and contains, at the surface,

36 SOURCES OF SUPPLY OF BISMUTH ORES

wolframite, arsenopyrite, some mineral phosphates and arsenates; at a depth of 65 ft. in a less altered zone the lode consists of a mass of pyrite slightly cupriferous and bismuth-bearing, with scheelite, its alteration product, meymacite (hydrated tungstate of calcium and iron), a little cassiterite and arsenopyrite slightly cobaltiferous. The bismuth minerals present are native bismuth, bismuthinite, bismuth ochre and bismutite—the last being the principal ore. Some lead minerals, the carbonate, the sulphate, the chlorophosphate and the molybdate, occur in like amounts, as well as molybdenite.

In the upper parts of the lode the bismuth minerals contain a little arsenic, antimony, lead, copper, iron, etc., and on the other hand the other minerals all contain bismuth, arsenopyrite, amongst them from 1·62 to 6·58% bismuth. In the immediate neighbourhood of this lode are dykes of fine-grained granulite containing several minerals, including bismuthinite, pyrite, chalcopyrite and blende. The deposit was discovered in 1867; operations were suspended in 1883 after a small amount of bismuth had been produced.

A little bismuth is found in a tungsten deposit in Puy-les-Vignes, and Daubrée found it in a calcite geode in the iron ore at Framont in the Vosges [5/I, p. 780].

GERMANY

For a long time Saxony had the world monopoly in the production of bismuth, but the output has been insignificant in recent years. The ores are found mainly in the Upper Erzgebirge region at Schneeberg, Johanngeorgenstadt, Schwarzenberg, Altenberg, Annaberg, and Zinnwald, where they are in association with those of tin, cobalt and silver. Much detail about the geology of these districts is given in the Imperial Institute monographs, *Tin Ores* (1919, p. 80), *Tungsten Ores* (1920, p. 55) and *Cobalt Ores* (1924, pp. 36–9).

The most important bismuth-bearing district has been that of Schneeberg, which is centred about Neustädtel. A large number of small veins of silver-cobalt-bismuth ores in a quartz gangue occur in metamorphosed Cambrian schists resting on granite. Some veins are mainly of cobalt-bismuth ores, silver being almost entirely absent. The bismuth minerals present

include native bismuth (the commonest), bismuthinite, bismuth ochre, bismutite, *bismuth-linnæite* and *chelenite* (bismuth cobalt-pyrite) [43/p. 339] [5/I, p. 781]. The gossan of the cobalt-bismuth veins is 450 to 550 ft. deep and seldom as little as 250 ft. Bismuth ochre and other oxidized bismuth minerals are found in it, sometimes forming rich ore-bodies close to the surface. The vein filling is mostly massive, but is sometimes banded [43/p. 345].

In some parts of the Schneeberg district bismuth is found in arborescent form in brown jasper, which has been occasionally cut and polished for small ornaments [2] (compare p. 22).

The silver-cobalt lodes of Annaberg, which is east of the Schneeberg district, contain native bismuth and bismuthinite. In the Fichtelgebirge bismuth is associated with cobalt and nickel ores. In the neighbourhood of Johanngeorgenstadt there are silver-cobalt-bismuth veins near metalliferous greenstones [44/p. 418].

Native bismuth is found in the many tin-tungsten veins of Saxony, especially those in the Altenberg district.

Near Nassau are quartzose lodes in ancient volcanic tuffs and picrites, containing bismuth ore in addition to siderite, ankerite and copper- and nickel-bearing pyrites [46/p. 217].

Outputs of bismuth ore for 1918 and 1919 from various districts of Saxony, whose tenor is unknown, in metric tons were :

	1918.	1919.
Johanngeorgenstadt . . .	118	66
Schneeberg . . .	153	122
Altenberg . . .	31	9

[45].

At Wittichen in the Black Forest bismuth is met with in a gold-cobalt lode, which is in granite country, and at Schutzbach, further north in the Siegen district of Prussia, bismuth is found in association with sulphide ores of nickel, iron and copper in Devonian rocks [5/I, p. 781].

NORWAY

Bismuth occurs in some of the six Scandinavian cobalt fahlbands, but always in small amount ; in other cases it is absent. The fahlbands, which contain cobalt arsenides, are

38 SOURCES OF SUPPLY OF BISMUTH ORES

described in the Imperial Institute monograph, *Cobalt Ores* (1924, pp. 39-40).

At Svartdal, N.E. of Møgen, Telemarken, in an area three miles long of ancient quartz-diorite, are transverse tourmaline-quartz veins, which carry a fair amount of bismuthinite, native bismuth and, occasionally, some tetradymite, with native gold, pyrite, chalcopyrite, and, in places, galena [6/pp. 637, 1136, 1140].

Bismuth is associated with copper ores near Drammen, and at Kjennar in the County of Lier are important bismuth mines [36/p. 244].

SWEDEN

One of the three types of deposit found at Falun in Sweden is rich gold ore in quartz, which is accompanied by a seleniferous bismuthinite-galena containing 51% bismuth and 14% selenium. The gold is found almost exclusively in the immediate neighbourhood of the selenium mineral, and by hand-sorting it is possible to separate one product containing 10-30% selenium and another with 3-10 oz. gold per ton.

Bismuth in small amount occurs in some deposits of the Swedish cobalt fahlbands [6/pp. 314, 1140].

RUMANIA

Native bismuth is found at Cziklova in the Banat [31/p. 352], and tellurides of gold and silver are associated with tellurides of bismuth at Rezbanaya in S.W. Transylvania [5/I, p. 781].

RUSSIA

Bismuth-gold approaching maldonite in composition is found in the bismuth-telluride ores of Schil-Isset in the Urals, Russia.

SPAIN

A small amount of bismuth (0.37%) is found occasionally amongst the ore minerals at Rio Tinto, Spain, but no recovery has been reported [5/II, p. 673].

A British syndicate¹ commenced to mine bismuthinite and

¹ From information supplied by Mr. E. J. Bayliss through *British Chamber of Commerce in Spain*.

SPAIN

39

bismutite ores in 1905 in the district of Conquista, in the Province of Cordoba, and in the period to the end of 1914 had shipped 597.95 metric tons of dressed ore to the United Kingdom. On account of various difficulties the syndicate finally suspended operations in the beginning of 1915. The mine is now (1924) being unwatered by a Spanish company preparatory to resuming operations.

As a result of prospecting for bismuth during the war, induced by high prices, Spanish miners have taken up other concessions in the neighbourhood.

Before closing down its mine the British syndicate had begun to produce refined metallic bismuth. Guided by the results of their experience the Spanish firm of J. Alcantara started a refining works and is the purchaser of all ores produced in the neighbourhood.

The outputs of dressed bismuth ore in Spain, given in the table on page 21, were all produced in the Conquista district.

SWITZERLAND

In the Val d'Anniviers in the Canton of Valais, Switzerland, near Sierre, are some bedded veins containing native bismuth in association with cobaltiferous arsenopyrite, cobaltite and chloanthite [5/II, p. 598].

YUGO-SLAVIA

Amongst the mining operations carried on by the Germans in Serbia, during the war, was the preliminary exploration of a bismuth deposit at Gradiste, 9 miles south of Knjazevac in Serbian Macedonia. No recent information is available [47].

Bismuthinite occurs at Aldinats, about 10 miles east of Knjazevats, in quartzose veins in association with ores of copper. About 5½ miles south of Knjazevats, bismuth ores occur at Aljin Dol and Jasikova in association with chalcoppyrite, siderite, blende, pyrrhotite and arsenopyrite. Malachite and bismuth ochre are secondary. The veins are in gabbros in intimate association with later intrusive dolerite ("diabase"). Only exploratory work has as yet been undertaken in this promising district [48].

40 SOURCES OF SUPPLY OF BISMUTH ORES

ASIA

CHINA

Geological conditions of China are very imperfectly known, so that no general conclusions on ore deposits can be formulated.

Important discoveries of bismuth free from copper and arsenic have been recently made in Southern China in association with tungsten in the wolframite placer deposits. A little bismuth ochre has been produced in the south of Kiangsi Province, but the ore, bismutite and bismuth ochre, chiefly found in association with wolframite, is produced in the Wong Yuen, Yuigte, Pao Au, Shiang Shau and Chin Chow districts of Kwantung Province, from which over 5% of the entire world production is being produced. The deposits are on the surface and worked by coolies, who are provided simply with grass hooks and two enamelled basins each [49]. This is the same method of recovery as is employed in the case of the wolframite deposits. The ore is sent to the larger cities of Changsha, Swatow and Canton, where it is accumulated and whence it is sent mostly to Hong Kong for shipment to the market. Statistics of production are lacking, but from Hong Kong exports in bags of 112 lb. were 1,401 in 1920 and 1,258 in 1921. Fully 60% of the exports go to Liverpool; the balance, to San Francisco, Yokohama and Hamburg [45].

The exports to San Francisco for the first eight months of 1920 were 7,014 lb., against 11,544 lb. for the corresponding period of 1919 [50].

The ore is usually sold at a flat rate at a price arranged between buyer and seller and depending upon grade and quality.

At Hong Kong in October, 1921, the price for 45% bismuth ore was about sixty gold Hong Kong dollars per 100 lb. It has been as low as \$15. It is stated that only about 10 tons per month of 45% ore is allowed on the market by the Bismuth Association.

Ore and concentrates exported from Canton are reported to contain 50 to 65% bismuth. Exports in 1919 and 1920 were respectively 266 lb. only and 32 short tons.

Exports of ore from Swatow contain on an average 60% bismuth. In 1919 and 1920 they amounted to 59 and 54 short tons respectively [45].

DUTCH EAST INDIES

In the Dutch East Indies bismuth minerals have been found, but not in appreciable quantities, at Lake Toba in the Island of Samosir; in Banca; in Western Borneo and in Western Celebes [51].

JAPAN

There are many scattered occurrences of bismuth ores in Japan, chiefly native bismuth and bismuthinite. The ores are often associated with those of tungsten and molybdenum, and sometimes with gold and silver or copper.

The ore-bodies exist either as veins or as contact-metamorphic deposits. In the former the ore is usually associated with gold, silver or copper, and occurs in granitic or liparitic rocks; in the latter it is found commonly with ores of tungsten and molybdenum in rocks of the older geological formations.

The following is a table of the chief occurrences:

<i>Mines.</i>	<i>Provinces.</i>	<i>Deposits.</i>	<i>Geology.</i>
Nishizawa . .	Shimotsuke	Vein	Liparite
Nakanosawa . .	Yechigo	"	"
Ikuno . .	Tajima	"	"
Imo-oka . .	Mimasaka	"	Granite
Hade . .	"	"	"
Tomikuni . .	Tamba	"	"
Kamioka . .	Hida	Contact-metamorphic deposit.	Gneiss, limestone, near quartz-porphry

The Nishizawa is a gold-silver mine, formerly a producer of bismuth. Bismuthinite is found in it only in a rich pocket with argentite. In the Nakanosawa, also a gold-silver mine, from which bismuth has been produced, bismuthinite occurs in separate veins, which traverse and run parallel with the gold veins. In the Ikuno mine at Kanagase a small quantity of bismuthinite occurs in copper ore. In the mines Imo-oka, Hade and Tomikuni this mineral is associated in limited amount with chalcopyrite. A small production of 1,041 lb. dressed ore containing 25% bismuth has been recorded. The Kamioka is a silver-lead mine, but no bismuth in the ore is

42 SOURCES OF SUPPLY OF BISMUTH ORES

visible to the naked eye although the lead produced contains 0.2% bismuth.

The Kosaka is a silver-copper mine in Rikuchu Province. There is one record of production from it of 787 lb. metal, containing 95.2% bismuth, worth £345 [52].

The outputs of bismuth ore and metal given in the table on page 21 are almost entirely from the Kamioka mine.

KOREA (CHOSEN)

Copper-bismuth-gold deposits have been formed by the metamorphosis of sedimentary rocks by granite intrusions, in the Suan Mining Concession, Hwang Hai Province, Korea. At the Suan mine, at Hol Kol, there are two distinct types of ore-bodies, the Eastern and the Western, in both of which bismuthinite occurs in small amount in association with chalcopyrite, gold and silver. Further details are given in reference [53].

SIBERIA

Deposits of bismuth ore have recently been found in Siberia between Olovyana and Berezov, about 100 miles from Chita, but only about 5 miles from the railway. They were inspected by K. A. Nenadkevich, who with simplest apparatus produced 1,100 lb. bismuth at a cost of about 3s. 6d. per lb. [54]. A new mineral, "bazovismutit" (base bismutite) containing 60% bismuth has been found by Nenadkevich in the Zabaykalye region [55].

NORTH AMERICA

MEXICO

Bismuth minerals occur with other ores in a number of places in Mexico, but only in two of them has any production been recorded.

In the State of *Guanajuato* bismuthinite is found in the León, San Luis de la Paz and Guanajuato districts. Guanajuatite, a selenide of bismuth (Bi_2Se_3) is found in the Santa Catarina mine and in the Cavillo mine in the Sierra de Santa Rosa of the Guanajuato district. Silaonite (*see* p. 3) is found

in the Silao and Guanajuato districts. Tetradyomite (Bi_2Te_3) occurs in the León district.

In the San Antonio mine, San Rafael District, Sierra de Tapalpa, in the State of *Jalisco*, is an occurrence of *tapalpita*, a sulpho-telluride of bismuth and silver, probably of the formula $3\text{Ag}_2(\text{S},\text{Te})\cdot\text{Bi}_2(\text{S},\text{Te})_3$. Tetradyomite also occurs in the State.

In El Doctor veins at Cadereita, in the State of *Querétaro*, bismuthinite occurs, whilst in the Sierra de Querétaro, close to the State of San Luis Potosi, bismuth ochre is found.

The principal Mexican producer has been the Bismuth King silver mine, in the Cosalá district of the State of *Sinaloa*. The deposit is reported to contain 2% bismuth as cosalite with other ores [55A/p. 486].

In the State of *Sonora* bismuthinite occurs in an intergrowth with copper sulphides and heavy silicates in a contact-metamorphic garnet zone in the West Cananea mine [4/p. 415]. In the same state the Belen mine has been a large producer of bismuth.

In the State of *Zacatecas* bismuth minerals are found in the Ojo Caliente and Zacatecas districts. Native sulphide of bismuth occurs in the Cristo mine in the latter district [56].

UNITED STATES

Although bismuth ores are found in many places in the United States, the metal has only been produced as a by-product in the smelting of lead, copper, gold and silver ores. There have been but few discoveries of bismuth minerals in recent years.

In the Territory of *Alaska* are some interesting occurrences of bismuth minerals, but so far there has been no production. Native bismuth and bismuthinite are abundant in some specimens from Eva Creek [57].

On Charley Creek, two veins about 12 and 8 in. in thickness and separated by 16 to 18 in. of schist were found occurring in strike joints dipping 50° to 60° , and carrying a small proportion of bismuth [58]. Later, a 4-ft. quartz vein was

44 SOURCES OF SUPPLY OF BISMUTH ORES

explored which carried 15% bismuth and a fair gold content. Native bismuth and bismuthinite occurred in dull white and grey quartz [59].

On the Granite Hill claim, on the ridge between Melba and Monte Cristo creeks, near Fairbanks, is a bismuth-bearing gold quartz vein. The bismuth occurs native and as bismuthinite. Particles of visible gold are plentiful, embedded in the bismuth or quartz. Tellurium is present [60]. On the adjoining Monte Cristo claim, two quartz veins from 3 to 18 in. thick are in shattered porphyritic biotite-granite and carry gold, scheelite and bismuthinite, with traces of tellurium. The gold is intergrown with the bismuth minerals [61].

Bismuth ore was produced in the Silver district of Yuma Co., *Arizona*, in 1920 [50].

Bright native bismuth is found in lepidolite in the pegmatite veins of Rincon, San Diego Co., *California*. In Nevada City a small quantity of tetradyrite has been found in the concentrate from the Providence mine [4].

In the State of *Colorado* bismutite and bismuthinite are associated with lead-silver sulphide ores at Leadville. The ore-bodies contain erratic pockets of ore rich in bismuth. When such ores are obtained they are smelted separately to get a lead rich in bismuth, which is refined at the Omaha refining plant in Nebraska [62].

Bismuth has been mined at Leadville in the Highland Mary mine. Anhydrous bismuth carbonate is found at Mt. Antero, Chaffee Co., and is probably an alteration product of bismuthinite. Cosalite is found in the Comstock mine near Parrott City, La Plata Co., in a quartz vein with pyrite, blende, a telluride (sylvanite?) and native gold; also in the Gladiator and Alaska mines, and in the Yankee Girl mine at Red Mt., San Juan Co. [4].

Native bismuth occurs near Trumbull, *Connecticut*, in a quartz vein in association with marcasite, blende, galena and arsenopyrite.

Bismuto-sphærite, pseudomorphous after bismuthinite is found at Williamantic, associated with garnet and albite [4].

Bismuth in association with gold is found at Dahlonga and at Ashbury, or Asbury, in the State of *Georgia* [5/III, p. 492].

Bismuthinite has been found near the town of Cooper, 22 miles S.W. of Calais in the State of *Maine*.

Tetradymite occurs in garnetiferous rock in the Dolcoath mine, *Montana*, at Elkhorn [4].

In the Goldfield district of *Nevada* bismuthinite is found intergrown with free gold, when it is considered to be a favourable indicator for gold. It is also irregularly crystallized with quartz and pyrite. Stellate and sheaf-like forms of bismuthinite are common [4]. Other associated minerals besides native gold are pyrite and an arsenical farnatinitite, with small amounts of enargite, various tellurides, goldfieldite, chalcopyrite, galena, blende, pyrrargyrite and proustite, all in a flinty quartz gangue. Most of the fissures in which these minerals occur are in intrusive dacite, but a few are in andesite or other rock [63].

In the oxidized zones at Goldfield bismuth ochre is often associated with limonite; it also occurs as a pseudomorph after bismuthinite. Although bismuthinite is apparently the original bismuth mineral in the ore the bismuth has evidently migrated somewhat since the oxidized forms are not always pseudomorphs [4] [6/p. 568]. An analysis of some rich ore from the Mohawk mine at Goldfield gave the following percentages: Silica, 66.30; alumina, 9.09; magnesia, 0.24; copper, 2.08; iron, 3.83; bismuth, 0.35; tellurium, 2.42; sulphur, 6.30; gold, 2.00; silver, 0.25 [63].

At Hilltop, 14 miles S.E. of the Battle Mt. mine, bismuthinite is found in rich gold ore in quartzite. On oxidation near the surface the bismuthinite is encrusted with bismuth ochre [4]. There was a small production of bismuth ore from the Eureka and Pioche districts in 1920 [50].

In *New Mexico* bismutite has been mined at Engle, where it is associated with malachite and scheelite [4].

Bismuth minerals are found at Larne's mine, Munro, and at Brewer's mine in the Chesterfield district of *South Carolina* [64].

The dusts obtained by the Cottrell precipitation plant at the copper smelter at Garfield, *Utah*, are rich in bismuth. This is extracted at the Omaha refinery in *Nevada* [62]. Bismuthinite exists in the granite district of Beaver Co. with garnet and barytes, "a remarkable association of minerals"

46 SOURCES OF SUPPLY OF BISMUTH ORES

(Dana). It has also been found in the St. Mary's mine in the San Francisco region.

Native bismuth and bismutite are found in association with barytes and quartz in the Boss Tweed mine, in the Tintic District, the bismutite having radial growths similar to the bismuthinite at Goldfield, Nevada. In the Emerald mine in the same district at a depth of 500 ft. a fragment of limestone was coated with delicate crystals of native bismuth [4].

Cosalite is found in the ore zone of the Cactus mine in the San Francisco region, where, at the seventh level, it is contemporaneous with siderite and anhydrite [4].

The Sells mine at Alta produced ore containing 8,517 lb. bismuth in 1920, part of which with the silver and copper in the ore was paid for by the smelting company. Most of the ore was oxidized, but several lots of rich bismuthinite ore were shipped [50].

Near Loon Lake, Stevens Co., State of *Washington*, argenterous cosalite is found in quartz veins in mica-schist, near granite. Associated with it are hübnrite and galena [4].

In *Wyoming* a small vein of bismutite occurs in the Jelm Mts., Albany Co. [4].

The output of bismuth in the United States is derived from the refining of lead, tin and blister copper; from flue dust containing lead and bismuth, recovered at copper smelters by Cottrell treaters, and from crude lead and copper ores, containing bismuth, usually sold for their gold and silver contents. A few companies have produced refined bismuth in the past, but at the present time there are only two companies in operation: The United States Silver-Lead Refinery Co., with a plant at Grasselli, Indiana, and the United States Smelting and Refining Co., with a plant at Omaha, Nebraska, which has been mentioned above. The Betts process of lead refining is used at both plants; it has been developed by William Thum to recover bismuth, tellurium and antimony in addition to the refined lead. The United States Silver-Lead Refinery Co. owns the rights to a process for extracting bismuth by leaching the ore with brine containing an acid. The bismuth is dissolved by the acid and its solution is subse-

quently precipitated [45]. At the Omaha refinery, in addition to lead-bismuth products, crude bismuth, derived from the treatment of electrolytic tin-refinery slimes and shipped from the company's Perth Amboy plant, is also refined [65].

The refined bismuth is usually of great purity, and absolutely free from arsenic when used for pharmaceutical products.

The chief sources of bismuth recovered from lead in the United States are the Western States and Mexico [65].

Bismuth ore is usually paid for at the rate of 50 cents to \$1.25 per lb. of bismuth for ores with 3% bismuth or over, and at 75% of the market value for other metals. Usually only a small percentage of the bismuth contained in the ores going to lead smelters is recovered in lead bullion [50].

It is not possible to give exact figures of production of bismuth in the United States as the refining companies as a rule withhold the information. The production largely satisfies the demand, which is seasonal, being largest in the spring and summer and amounting to between 200,000 and 300,000 lb. annually [65]. The balance of the demand is largely met by importations from England, South America, China, etc.

Details of imports are given in the following tables :

Imports of Bismuth into the United States for 1917 showing Countries of Origin

	Lb.	Value.
England	38,453	\$103,684
Argentina	6,674	16,757
Chile	21,799	17,792
Uruguay	2,324	4,067
	<u>69,250</u>	<u>142,300</u>

[66].

Total Imports of Bismuth into the United States

	Quantity lb.	Value \$.		Quantity lb.	Value \$.
1913	151,030	257,176	1919	76,539	228,376
1914	133,190	241,448	1920	75,781	97,489
1915	34,237	72,587	1921	94,085	114,891
1916	64,821	155,925	1922	121,505	239,777
1917	88,465	196,113	1923	62,640	146,178
1918	85,611	208,098	1924	—	—

48 SOURCES OF SUPPLY OF BISMUTH ORES

According to the Department of the Interior, the quantity of bismuth sold in the United States in 1922 was 226,385 lb., and the average selling price was \$2.26 per lb. [65].

The American quotations for bismuth are the equivalent of the London prices, fixed by the Bismuth Association in London, after making allowance for foreign exchange, import costs, and at times duty. The present amount of the duty under the Fordney Act of 1921 is 25% *ad valorem*, in place of 10% under the Underwood law.

SOUTH AMERICA

ARGENTINA

In the Province of La Rioja at Los Coloraditos in a southern spur of the Sierra de Velasco extending into the Famatina Valley in Argentina are a number of quartz veins of average width 16 in., striking N.-S. and dipping E., which carry much tourmaline, with which is associated wolframite, and, in lesser quantity, bismuthinite, magnetite, pyrite, chalcopyrite, molybdenite and their oxidation products. The veins occur in the marginal facies of a muscovite-biotite-granite at its contact with biotite-gneiss, which is intersected by many pegmatites with large tourmaline crystals [67].

In the Sierra de San Luis, in the province of the same name, bismutite occurs in a vein containing also lime and manganese carbonates [4].

The production of bismuth ore in Argentina is very small.

BOLIVIA

Bolivia has for a long time been the principal producer of bismuth ores in the world, and could easily supply all the demand for them. The ores are in all cases associated with those of tin, but are not so widely distributed, occurring mainly in a few definite localities in the departments of La Paz and Potosí, the deposits all being on the Cordillera Real or eastern branch of the Andes.

Bismuthinite is the commonest ore mineral, but native bismuth predominates in a few cases, and bismuth ochre is found in the oxidized portions of the lodes, generally encrusting the other bismuth minerals. The ores consist largely of bismuth intergrown with cassiterite. Besides cassiterite and silver minerals, wolframite is often found, and also the minerals usually associated with tin-silver ores, viz. pyrite, and other iron ores, sulphides of copper, lead and zinc with quartz, siderite and barytes and, occasionally, tourmaline. The cassiterite is often much intergrown with bismuthinite. The ores are generally connected with dykes of dacite and quartz-trachyte traversing altered clay-slates [46/p. 218].

Potosí.—The most important bismuth-producing mines in Bolivia are those of a Swiss company, the Compagnie Aramayo de Mines en Bolivie, and which consist of two groups at Tasna and at Chorolque, in the provinces of North and South Chichas, near Atocha, in the Department of Potosí. The areas controlled at these places by the company, in addition to others, are 3,608 and 2,019 acres respectively.

At Tasna bismuthinite is the principal ore. The deposits are among the largest known. Tasna Mt., on which they are found, dominates a group of hills, almost entirely of slate, but cut by many rhyolite dykes. Although mineralization extends to the neighbouring hills, it is mainly confined to Tasna Mt. There is a large number of veins, but their filling varies at different points.

On the east side of the mountain are the most important bismuth veins, in which besides bismuthinite are pyrite, arsenopyrite, hæmatite, quartz and, in lesser amounts, argentiferous galena, stibnite, siderite and molybdenite. On the south side are veins of arsenopyrite, with some cassiterite, but less bismuthinite. On the west side is an intersecting vein system in greywacke, the veins varying in dip and strike and in width up to 3 ft. The vein contents are bismuth and tin ores, one or the other predominating, with small amounts of other metallic minerals in a gangue of quartz and clay. On the north side are narrow bismuth-antimony veins only. The upper part of the mountain is highly silicified, and contains veins of tungsten, tin and bismuth ores, and arsenopyrite.

50 SOURCES OF SUPPLY OF BISMUTH ORES

Apatite occurs sparingly, but tourmaline, abundantly, in Tasna ores. The ores are both concentrated and smelted at Buen-Retiro [67/p. 130].

The Chorolque deposits are on the mountain of the same name, which is 3,000 ft. above the surrounding country and of 20,000 ft. altitude. It consists of a pyramid of quartz-trachyte or quartz-andesite, which has cut through the series of shale and quartzite which outcrops on the side of the mountain. At the contact is a breccia of silicified rock, especially rich in tin. The metalliferous veins occur in the igneous rock, which has been considerably silicified. There is much variation in the filling of the veins, the ores being those of silver, tin, tungsten and bismuth. In some veins one metal only is present; in others, several. Generally the tin ores are found near the summit; those of silver, at lower levels, whilst bismuth ores are the lowest. The veins, of average width about 3 ft., strike E.-W., and dip S., but the dip varies. The vein-walls are not well defined. The tin ores have been mined the most.

The more complex ores carry pyrite, chalcopryite, blende, galena, tetrahedrite, besides bismuthinite and native bismuth. The gangue consists of quartz, barytes and siderite. In some cases wolframite is present.

The gullies leading from the mountain all contain rich alluvial deposits.

The company operates two groups of mines on this mountain, one, the older Chorolque group with some workings at an altitude of 18,000 ft., and another group, on the other side of the mountain. The company has concentrating plants at Sta. Barbara, Sta. Elena and Sala Sala, and a smelter at Quechisla for treating its Chorolque ores.

A subsidiary company, the Anglo-Bolivian Mining Syndicate, Ltd., operates bismuth and other mines in the Potosí district.

In the Province of Bustillo, Potosí, on the S.E. slope of the Cerro Llallagua, are the famous Uncia tin mines, known as La Salvadora, and owned by Simon I. Patiño y Cia. The mountain consists of a central mass of quartz-porphyry, which has been intruded through a thick series of slates and

shaly sandstones. Numerous quartzose stanniferous veins cut through both igneous and sedimentary rocks, but the workings are confined to the former. The veins are very varied in width, averaging only about a foot in thickness. Besides cassiterite, they contain pyrite in abundance, wolframite, scheelite, arsenopyrite, siderite and other minerals. Bismuthinite occurs in the ore, considerably in the Inca and One A veins, but it only recently received attention [67/p. 119].

The Llallagua mines, also Chilean-owned and famous for their production of tin, are situated on the N.E. side of the same mountain and are contiguous with the Uncia mines. The geology of the deposits is similar. Some of the Uncia veins pass into the Llallagua mines, and are also worked in them, including the One A, which continues to be bismuth-bearing [67/p. 120]. The company completed a plant for the extraction of bismuth from tin concentrate in 1923, when its production was about 8 tons of 99% bismuth per month [68].

La Paz.—In the Department of La Paz, about twenty miles north of the city of the same name on the flanks of the Huayna-Potosí Mt. (20,000 ft.) is a group of bismuth-tin mines, the Carmen, the Esperanza and the San Alberti near La Union, which are worked by a French company.

The rocks of the region consist of black arenaceous slates, micaceous sandstones, and Devonian quartzites, which have been intruded by dykes of quartz-porphyry and similar rocks. The sedimentary rocks rest on granite, the slates and quartzites striking N.-S. and dipping 5°-50° W. The veins occur in shattered zones that approximately conform in strike with that of the enclosing slates and quartzites, but generally dip steeply to the east.

The Carmen is the most important mine. Much of the ore occurs in stringers in the quartzite, where there has been considerable shattering of the rock. The greatest amount is found in the quartzite along its contact with overlying slate. In the ore bismuth minerals are of more value than the tin, and, contrary to the usual experience elsewhere in Bolivia, native bismuth predominates in amount over that of the other minerals, bismuthinite and bismuth n some

52 SOURCES OF SUPPLY OF BISMUTH ORES

cases the native bismuth is surrounded by a band of bismuthinite, but more commonly the two minerals alternate in radiating bladed forms, indicating contemporaneous origin. Besides cassiterite in the quartz gangue, there is much pyrite, with a smaller amount of silver and copper minerals.

The bismuth ores are hand-sorted into a first-class native product and a first-class sulphide product, both of which are shipped to Havre for treatment at Rouen. The remainder is sorted into a second-class product with 5 to 6% bismuth, which is either smelted locally or exported, according to market conditions, and a third-class product with 2 to 3% bismuth. The last is lixiviated, and the oxychloride of bismuth, which is recovered, is reduced to metal by smelting.

In 1915 there was a production of dressed bismuth ore equivalent to about 40 tons of metal [67/pp. 103-5].

At Japajopo, at the foot of the Huayna-Potosí Mt., are a number of tin placers in an area of 2,500 acres, in which native bismuth, bismuthinite, gold and other minerals are present. There are other placers at Francisco and Concepción, which are in the Province of Omasuyos and in the Canton of Pucarani. Flakes of bismuth of 98% purity are recovered in the concentrate won from these two placers [65/p. 381].

BRAZIL

Native bismuth and bismuth ochre are found in a number of gold mines in the Province of Minas Geraes, Brazil, especially in the Passagem deposit, about four miles east of Ouro Preto, and their presence prevents the employment of amalgamation for the recovery of the gold.

In the Passagem mine the presence of the bismuth ores with auriferous arsenopyrite in the interstices of tourmaline-bearing quartz accentuates the resemblance of this deposit to tin-bearing deposits elsewhere [5/III, p. 603].

Bismuth is reported to have been found in the State of Rio Grande do Sul [69/p. 70]; at Brijões (Areia) and at St. Antonio de Jesús in the State of Bahia [70].

CHILE

Native bismuth and bismuthinite, with chilenite and ores of other minerals containing a little bismuth, have been reported to occur in mines near Juan Godoy and San Antonio, del Potrero Grande, in the Department of Copiapó, Province of Atacama, Chile [67/p. 282].

PERU

In the Department of Junín, in the Colquijirca district, Peru, is the important San Gregorio bismuth mine, which is one mile east of Hauraucaca, where there is a dressing plant at which the ore is treated.

The mine is near the base of a sandstone hill about 150 ft. high rising out of the pampa. The sandstone varies in texture from fine- to coarse-grained, and the ore deposit is in a brecciated mass of it.

The ore consists entirely of oxidized bismuth minerals, chiefly the basic arsenate, and occurs in a yellow to brown clay filling the spaces in the brecciated sandstone, but also in places as light-yellow bismuth compounds in the fragments of sandstone. The crude ore contains 3% bismuth.

The ore-body has been worked as an open cut, 1,000 ft. by 80 ft. in area, but at a depth of 20 to 30 ft. the bismuth content becomes very low. The deposit might be the gossan of a lode, but no sulphide minerals of bismuth have been found, and the origin of the deposit is unknown.

Operations commenced in 1905. In the first ten years a market product containing 20% bismuth was produced by concentration, but 10,000 tons of 5% middling were accumulated. At the present time mining is temporarily suspended, and production is made from the middling. This is first roasted, and then leached with a strong solution of common salt and sulphuric acid; bismuth sulphide is precipitated from the solution by the addition of sodium sulphide, and bismuth is recovered from it by smelting. The mine possesses reserves of ore sufficient to supply the world's demand of about 300 tons of bismuth per annum for many years, but the

54 SOURCES OF SUPPLY OF BISMUTH ORES

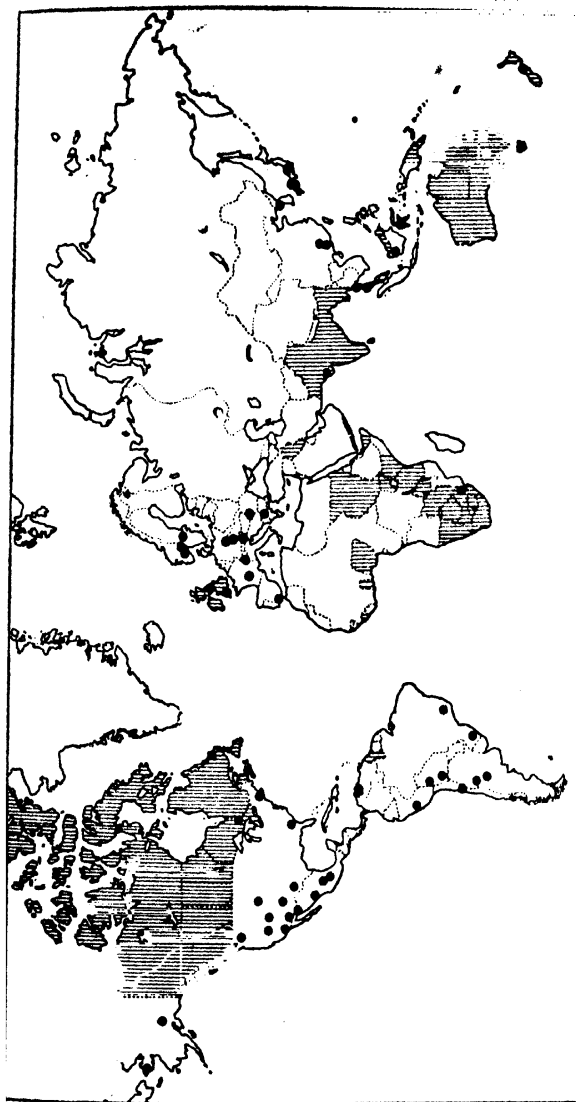
owners are party to an agreement with the Bismuth Association by which output is restricted to 25 tons [67/p. 432] [71].

In 1917, 14 tons of ore containing 3,285 lb. bismuth were shipped from the Regla mines near Cerro de Pasco, Junín [72].

In the Morococha district of Junín in the Matilde mine are bismuth minerals including the double sulphide of silver and bismuth, matildite (AgBiS_2) [5/I, p. 777].

VENEZUELA

Deposits of bismuth minerals are known near Tocuyo, in the State of Lara, Venezuela [67/p. 538].



MAP SHOWING THE BISMUTH-BEARING LOCALITIES REFERRED TO IN THE TEXT. (British Empire shaded.)

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